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(11) **EP 1 296 364 A1**

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

26.03.2003 Bulletin 2003/13

(51) Int Cl.7: **H01L 21/205**, H01L 21/31,
C23C 16/455

(21) Application number: **01943818.3**

(86) International application number:
PCT/JP01/05406

(22) Date of filing: **25.06.2001**

(87) International publication number:
WO 01/099165 (27.12.2001 Gazette 2001/52)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

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(30) Priority: **23.06.2000 JP 2000188821**

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(54) METHOD FOR FORMING THIN FILM AND APPARATUS FOR FORMING THIN FILM

(57) A shower head 9 having a plurality of ejection holes for supplying an organic metal gas at uniform density to the surface of a substrate 10 and a plurality of ejection holes for supplying an oxidizing gas at uniform density to the same is provided in a reaction furnace 8

of an MOSVD system. A heater for heating the inside to a temperature higher than the thermal decomposition point of the organic metal gas but lower than the film forming temperature is provided in the vicinity of the substrate-side surface of the shower head 9.

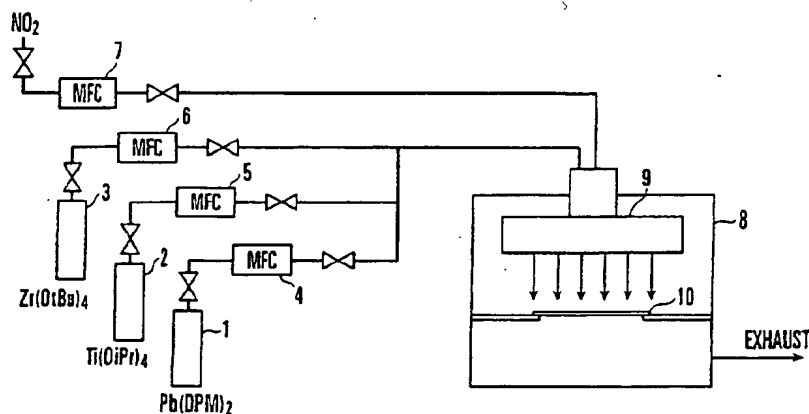


FIG. 1

Description

1. Technical Field

[0001] The present invention relates to a thin film forming method and thin film forming apparatus for forming a thin film containing a metal element on a substrate by chemical vapor deposition which utilizes the thermal decomposition reaction of an organometallic compound.

2. Background Art

[0002] An MOCVD (Metal Organic Chemical Vapor Deposition) has been conventionally known which forms a compound semiconductor film by utilizing the thermal decomposition reaction of an organometallic compound. This MOCVD can form a thin film made of a ferroelectric such as PZT, which is used in a semiconductor device such as a memory.

3. Disclosure of Invention

[Problem to be Solved by the Invention]

[0003] To form a thin film made of a ferroelectric such as PZT on a semiconductor device, a film must be formed at a low temperature of 450°C or less, and a sufficient film formation rate must be obtained. When a PZT film is to be formed, the uniformity in its composition must be ensured. In the conventional MOCVD, however, it is difficult to satisfy both the uniformity in composition of a thin film and a sufficient film forming rate.

[0004] In contrast, a technique for increasing the uniformities in composition and thickness of a thin film by using a shower head has been known. On the other hand, a technique for increasing a film formation rate by preheating an organic metal gas serving as a source gas and supplying it on a substrate has been known. There is thus provided a technique for preheating a source gas by a heater arranged between the shower head and a substrate in order to increase a film formation rate while using a shower head.

[0005] However, this technique has the following problem.

(a) In metal oxide film formation, an oxidizing gas is also supplied to the substrate as the source gas. In this case, when a heater is exposed, it is unfavorably oxidized.

(b) When preheating is performed near the gas introduction portion of the shower head, a highly reactive component is generated by preheating. Since this component easily attaches to the inner wall of the shower head, the nozzles of the shower head clog. In addition, when a multicomponent metal oxide film such as a PZT film is to be formed, since some components contained in the film are to

be easily deposited by preheating and others are not, the supply amount of only a certain component may be reduced.

5 [0006] For these reasons, when preheating is performed before film formation, the uniformities in thickness and composition of a film in film formation degrade.

[0007] The present invention has been made to solve the above problem, and has as its object to provide a
10 thin film forming method and thin film forming apparatus which can ensure the satisfactory composition of a thin film and the uniformity in thickness thereof, and increase a film formation rate.

15 [Means of Solution to the Problem]

[0008] In a thin film forming method of the present invention, an inside in the vicinity of a substrate-side surface of gas supply means for supplying an organic metal
20 gas to a surface of a substrate at uniform density is heated to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature.

[0009] As described above, the organic metal gas can
25 be supplied to the surface of the substrate at uniform density by using the gas supply means. Heating a local portion immediately before the position of uniform supply of the organic metal gas from the gas supply means enables the thermal decomposition of the organic metal
30 gas. In forming a thin film, e.g., a PZT film in which the uniformity in composition is very important, an intermediate product thermally decomposed without impairing the uniformity in composition can be supplied to the surface of the substrate. Therefore, a film formation rate
35 can increase without impairing the uniformities in thickness and composition of the film.

[0010] In another thin film forming method of the present invention, an inside at only a periphery of an
40 ejection hole for an organic metal gas, out of two gas ejection holes provided to gas supply means for supplying an organic metal gas and oxidizing gas to a surface of a substrate at uniform density, is heated to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature.
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[0011] As described above, since only the inside at the periphery of the ejection holes for the organic metal gas is heated to a temperature higher than the thermal decomposition point of the organic metal gas but lower
50 than the film forming temperature, the organic metal gas can be thermally decomposed, thereby supplying a thermally decomposed intermediate product to the surface of the substrate.

[0012] In a thin film forming apparatus of the present
55 invention, gas supply means having a plurality of ejection holes which supply an organic metal gas to a surface of the substrate at uniform density is provided in a reaction chamber, and a heater for heating the organic

metal gas to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature is incorporated near a substrate-side surface of the gas supply means.

[0013] As described above, the organic metal gas can be supplied to the surface of the substrate at uniform density by using the gas supply means. Heating, by a heater, a local portion immediately before the position of uniform supply of the organic metal gas from the gas supply means enables the thermal decomposition of the organic metal gas. In forming a thin film, e.g., a PZT film in which the uniformity in composition is very important, an intermediate product thermally decomposed without impairing the uniformity in composition can be supplied to the surface of the substrate. Therefore, a film formation rate can increase without impairing the uniformities in thickness and composition of the film.

[0014] In another thin film forming apparatus of the present invention, gas supply means having a plurality of first ejection holes which supply an organic metal gas to a surface of the substrate at uniform density and a plurality of second ejection holes which supply an oxidizing gas at uniform density are provided in a reaction chamber, and a heater for heating the organic metal gas to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature is incorporated around the first ejection holes of the gas supply means.

[0015] As described above, since the periphery of the first ejection holes is heated by a heater to a temperature higher than the thermal decomposition point of the organic metal gas but lower than the film forming temperature, the organic metal gas can be thermally decomposed, thereby supplying the thermally decomposed intermediate product to the surface of the substrate.

4. Brief Description of Drawings

[0016]

Fig. 1 is a block diagram showing the arrangement of an MOCVD system according to an embodiment of the present invention;

Fig. 2 is a bottom view of a shower head shown in Fig. 1;

Fig. 3 is a sectional view of the shower head shown in Fig. 1; and

Fig. 4 is a plan view showing the pattern of a heater.

5. Best Mode of Carrying Out the Invention

[0017] An embodiment of the present invention will be described in detail with reference to the accompanying drawings. Fig. 1 is a block diagram showing the arrangement of an MOCVD system according to an embodiment of the present invention.

[0018] In Fig. 1, reference numeral 1 denotes a source tank which holds a lead dibivaloylmethane com-

plex $\text{Pb}(\text{DPM})_2$; 2, a source tank which holds an organometallic compound source containing Ti, e.g., $\text{Ti}(\text{OiPr})_4$; 3, a source tank which holds an organometallic compound source containing Zr, e.g., $\text{Zr}(\text{OtBt})_4$; 4 to 7, mass-flow controllers for respectively controlling the flow rates of $\text{Pb}(\text{DPM})_2$ gas, $\text{Ti}(\text{OiPr})_4$ gas, $\text{Zr}(\text{OtBt})_4$ gas, and NO_2 gas; 8, a reaction chamber; 9, a shower head serving as a gas supply means; and 10, a semiconductor substrate.

[0019] In this embodiment, the shower head 9 is used as a means for supplying an organic metal gas and oxidizing gas to the substrate 10 at uniform density. Fig. 2 is a bottom view of the shower head 9, and Fig. 3 is a sectional view of the shower head 9.

[0020] The lower structure of the shower head 9 is constructed by AlN ceramic plates 11 and 12 with good thermal conductivity. The ceramic plates 11 and 12 have a plurality of first ejection holes 13 for ejecting an organic metal gas and a plurality of second ejection holes 14 for ejecting an oxidizing gas (NO_2 gas). A heater 15 having a shape shown in Fig. 4 is printed on the upper surface of the AlN ceramic plate 11, which is formed to detour the ejection holes 13 and 14. The ceramic plates 11 and 12 accordingly sandwich the heater 15 therebetween. The heater 15 generates heat by making a current flow therein, so that the ceramic plates 11 and 12 are heated to a temperature (e.g., 240°C when a PZT film is to be formed as in this embodiment) higher than the thermal decomposition point of the organic metal gas but lower than the film forming temperature.

[0021] In contrast, an upper structure 16 of the shower head 9 is made of Al. The upper structure 16 is heated by a heater (not shown) to a temperature (e.g., 200°C when the PZT film is to be formed) higher than a temperature at which the organic metal gas can keep the vapor state but lower than the thermal decomposition point of the organic metal gas. When a buffer plate (not shown) made of Al_2O_3 or the like which has thermal conductivity lower than that of AlN is then formed between the AlN ceramic plate 12 and upper structure 16, the AlN ceramic plates 11 and 12 can be kept at a temperature higher than that of the upper structure 16.

[0022] A thin film forming method using the above-described MOCVD system will be described next. First, the source tank 1 is heated to evaporate the lead dibivaloylmethane complex $\text{Pb}(\text{DPM})_2$, and the source tank 2 is simultaneously heated to evaporate an organometallic compound source $\text{Ti}(\text{OiPr})_4$. The resultant $\text{Pb}(\text{DPM})_2$ gas and $\text{Ti}(\text{OiPr})_4$ gas and NO_2 gas are introduced into the evacuated reaction chamber 8. At this time, the pressure of the reaction chamber 8 is 0.005 torr, the flow rate of $\text{Pb}(\text{DPM})_2$ gas is 0.2 sccm, the flow rate of $\text{Ti}(\text{OiPr})_4$ gas is 0.14 sccm, the flow rate of NO_2 gas is 2.3 sccm, and a film forming temperature (substrate temperature) is 445°C . Under these conditions, $\text{Pb}(\text{DPM})_2$ gas and $\text{Ti}(\text{OiPr})_4$ gas pass through a path shown in Fig. 3 and are ejected from the ejection holds 13, and NO_2 gas passes through a path shown in Fig. 3 and is ejected from the

ejection holes 14. With this processing, a crystal nucleus with a perovskite structure made of PbTiO_3 is formed on the substrate 10.

[0023] Successively, the source tank 3 is heated to evaporate $\text{Zr}(\text{OtBt})_4$, and the resultant $\text{Zr}(\text{OtBt})_4$ gas is introduced into the reaction chamber 8 together with the gases described above. The flow rate of $\text{Zr}(\text{OtBt})_4$ gas is 0.175 sccm, and other conditions are the same as in the above description. $\text{Zr}(\text{OtBt})_4$ gas is ejected from the ejection holes 13 together with $\text{Pb}(\text{DPM})_2$ gas and $\text{Ti}(\text{OiPr})_4$ gas. With this processing, a PZT film ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ film) with the perovskite structure is formed on the substrate 10.

[0024] In this embodiment, the organic metal gas and oxidizing gas can be supplied to the surface of the substrate 10 at uniform density by using the shower head 9. The gas pipes to the shower head 9 are kept at a temperature (160 to 200°C when the PZT film is to be formed) lower than thermal decomposition point of the organic metal gas, and the vicinity of the ejection holes 13 of the shower head 9 is heated to a temperature higher than the thermal decomposition point of the organic metal gas. With this processing, the organic metal gas which is easily thermally decomposed can be transported to the vicinity of the ejection holes of the shower head 9 and then thermally decomposed at the vicinities of the ejection holes 13. Therefore, the film formation rate can be made twice or more the conventional rate, from 10 nm/min to 25 nm/min. Note that the heater 15 heats both the ejection holes 13 and 14 in this embodiment. However, if the heater 15 heats only the vicinity of the ejection holes 13, the same effect can also be obtained.

[0025] Since the AlN has good thermal conductivity, variations in temperature of the substrate-side surface of the shower head 9 can be suppressed within $\pm 1^\circ\text{C}$, thereby obtaining the satisfactory uniformity in temperature. Thus, the satisfactory composition and uniformity in thickness of the thin film formed on the substrate 10 can be ensured, and the film formation rate can be greatly increased as compared with that in the prior art.

[0026] Note that a nucleus forming process and a film forming process are performed at a high vacuum of 0.005 torr in this embodiment, but the film forming process may be performed at a low vacuum. That is, the lead dibivaloylmethane complex $\text{Pb}(\text{DPM})_2$ and organometallic compound source $\text{Ti}(\text{OiPr})_4$ are dissolved in an organic solvent (butyl acetate solution) and evaporated together with the organic solvent, and the resultant gas is introduced into the reaction chamber 8 at a pressure of 0.005 torr to form a nucleus. Successively, the organometallic compound source $\text{Zr}(\text{OtBt})_4$ is dissolved in the organic solvent together with the above-described $\text{Pb}(\text{DPM})_2$ and $\text{Ti}(\text{OiPr})_4$ and evaporated with the organic solvent, and the resultant gas is introduced into the reaction chamber 8 at a pressure of about 0.1 to 0.5 torr to form a film. At this time, to make the respective partial pressures equal, an inert gas is introduced so as to make a total flow rate of gases about 20 to 100 times.

This can increase the internal pressure of the shower head 9, thereby uniformly supplying the organic metal gas to the surface of the substrate.

[0027] This embodiment uses the post-mix type shower head 9 which supplies the organic metal gas and the oxidizing gas independently. However, a pre-mix type shower head for supplying the organic metal gas and oxidizing gas together may be used. In addition, the PZT film is formed on the substrate 10 in this embodiment, but the film is not obviously limited to the PZT film.

[0028] As described above, according to this embodiment, the inside of the vicinity of the substrate-side surface of the shower head 9 is heated to a temperature higher than the thermal decomposition point of the organic metal gas but lower than the film forming temperature. With this processing, the satisfactory composition and uniformity in thickness of the thin film formed on the substrate 10 can be ensured, and the film formation rate can be greatly increased as compared with that in the prior art. As a result, a thin film forming apparatus with good mass production can be realized. In addition, since the inside of the vicinity of the substrate-side surface of the shower head 9 is to be heated, the heater 15 is not exposed, thereby preventing the heater 15 from oxidation.

6. Industrial Applicability

[0029] As has been described above, the present invention is suitable to forming a high-quality thin film.

Claims

1. A thin film forming method of forming a thin film containing a metal element on a substrate by chemical vapor deposition which utilizes a thermal decomposition reaction of an organometallic compound, **characterized by** comprising heating, to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature, an inside in the vicinity of a substrate-side surface of gas supply means for supplying an organic metal gas to a surface of the substrate at uniform density.
2. A thin film forming method of forming a thin film containing a metal element on a substrate by chemical vapor deposition which utilizes a thermal decomposition reaction of an organometallic compound, **characterized by** comprising heating, to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature, an inside at only a periphery of an ejection hole for an organic metal gas out of two gas ejection holes provided to gas supply means for supplying an organic metal gas and oxidizing gas to a surface of the substrate

at uniform density.

3. A thin film forming apparatus for forming a thin film containing a metal element on a substrate by chemical vapor deposition which utilizes a thermal decomposition reaction of an organometallic compound, **characterized by** comprising
- gas supply means provided in a reaction chamber to have a plurality of ejection holes which supplies an organic metal gas to a surface of the substrate at uniform density,
- wherein a heater for heating the organic metal gas to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature is incorporated near a substrate-side surface of said gas supply means.
4. A thin film forming apparatus for forming a thin film containing a metal element on a substrate by chemical vapor deposition which utilizes a thermal decomposition reaction of an organometallic compound, **characterized by** comprising
- gas supply means provided in a reaction chamber to have a plurality of first ejection holes which supply an organic metal gas to a surface of the substrate at uniform density and a plurality of second ejection holes which supply an oxidizing gas at uniform density,
- wherein a heater for heating the organic metal gas to a temperature higher than a thermal decomposition point of an organic metal gas but lower than a film forming temperature is incorporated around the first ejection holes of said gas supply means.

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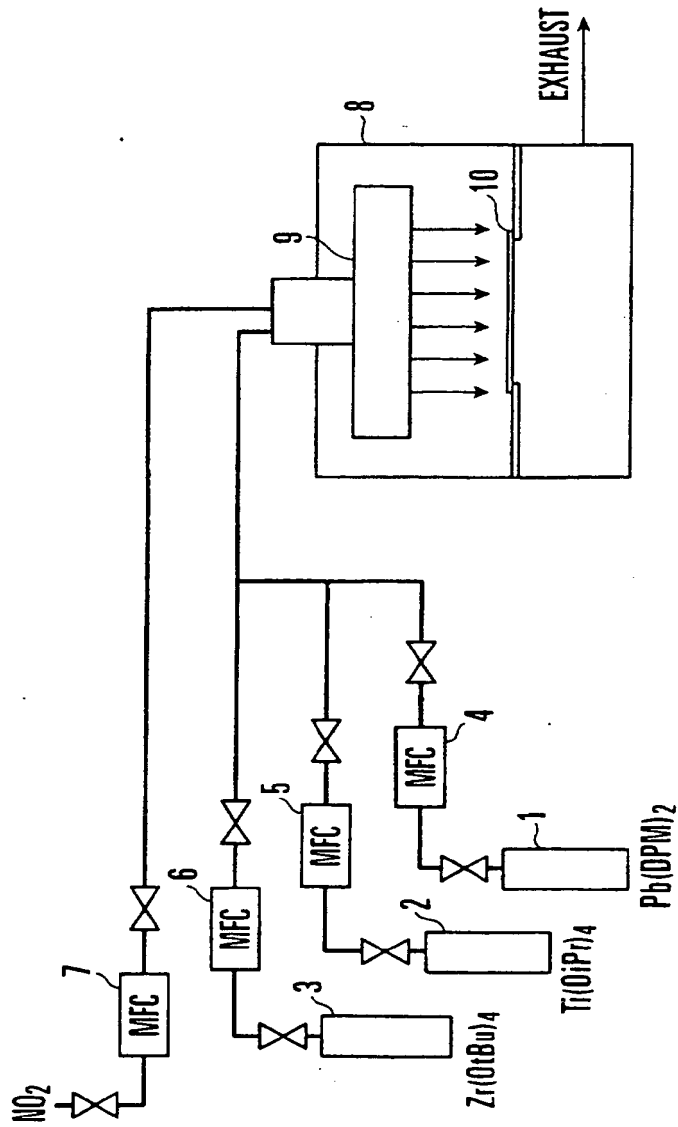


FIG. 1

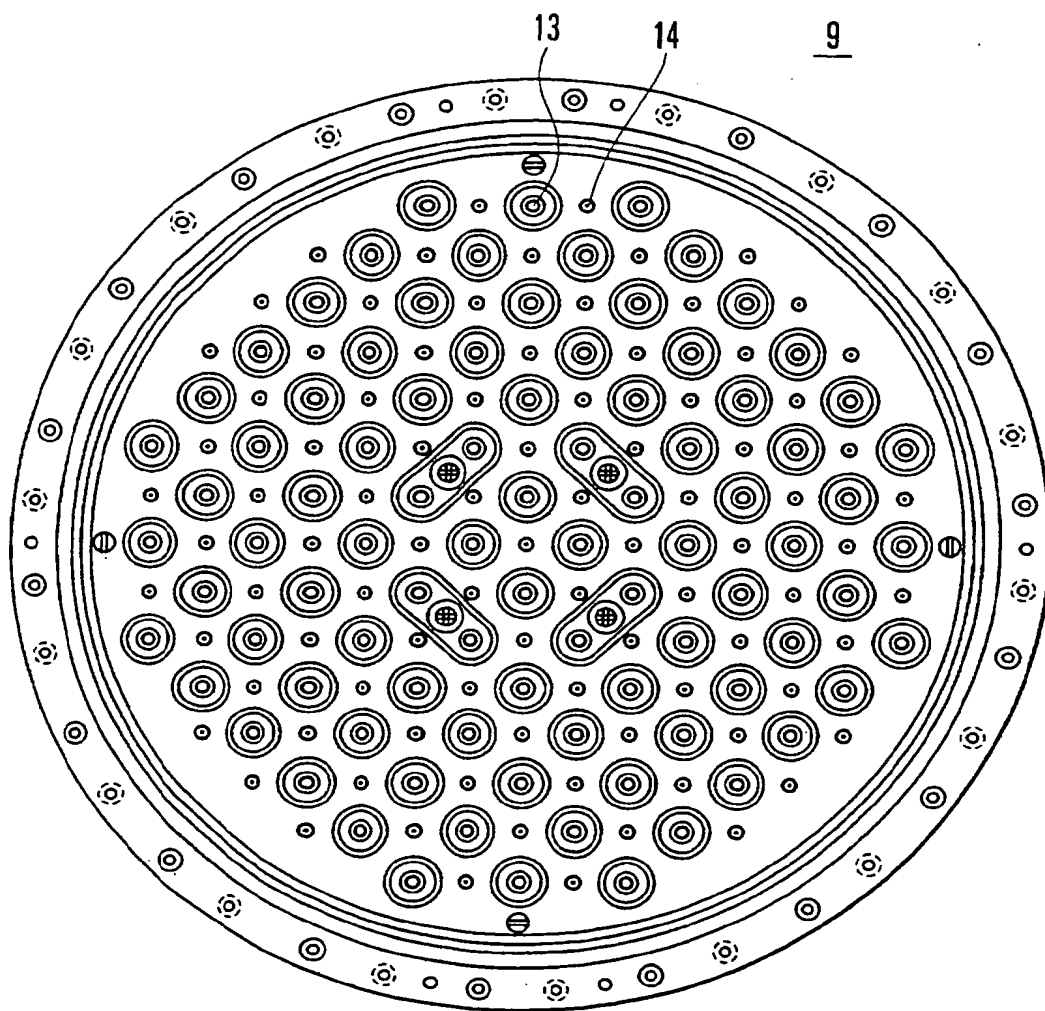


FIG. 2

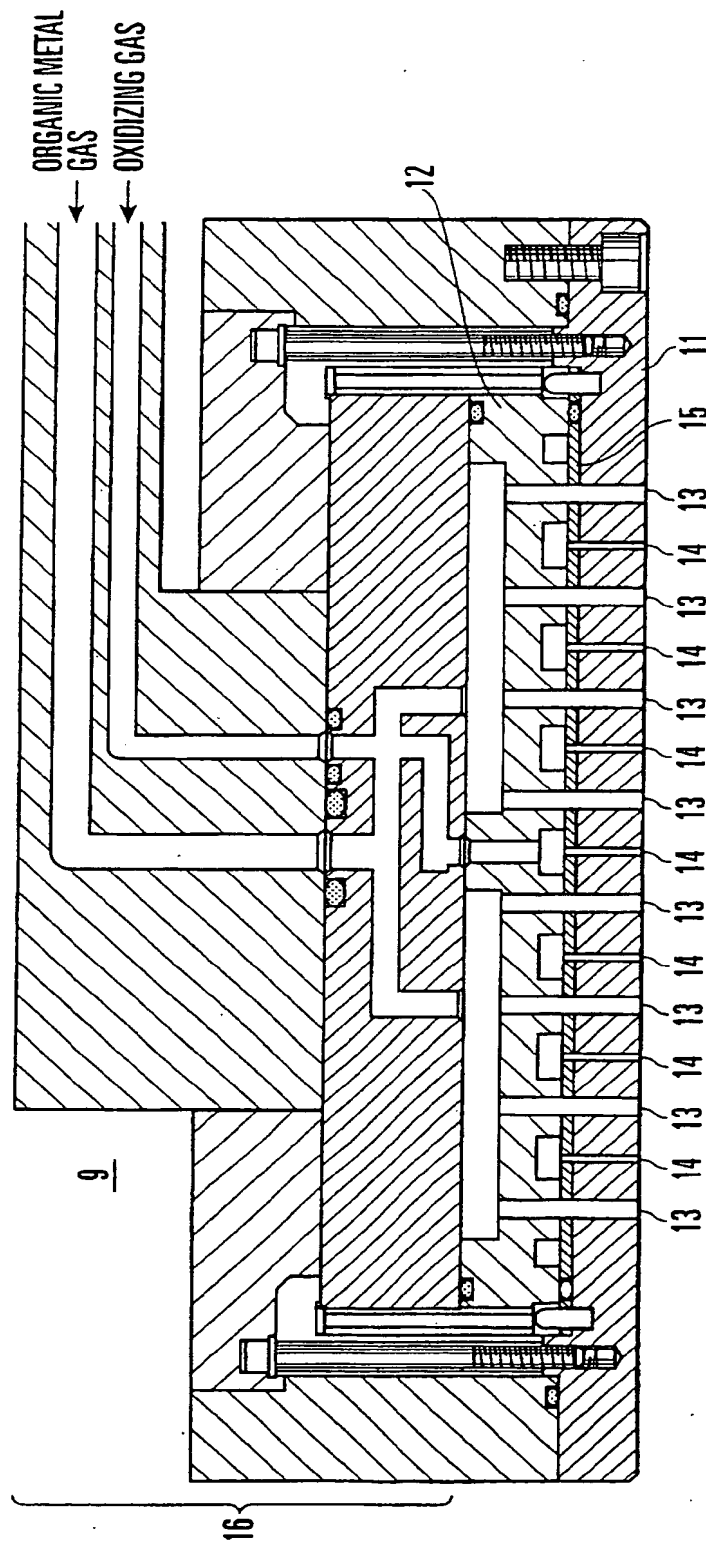


FIG. 3

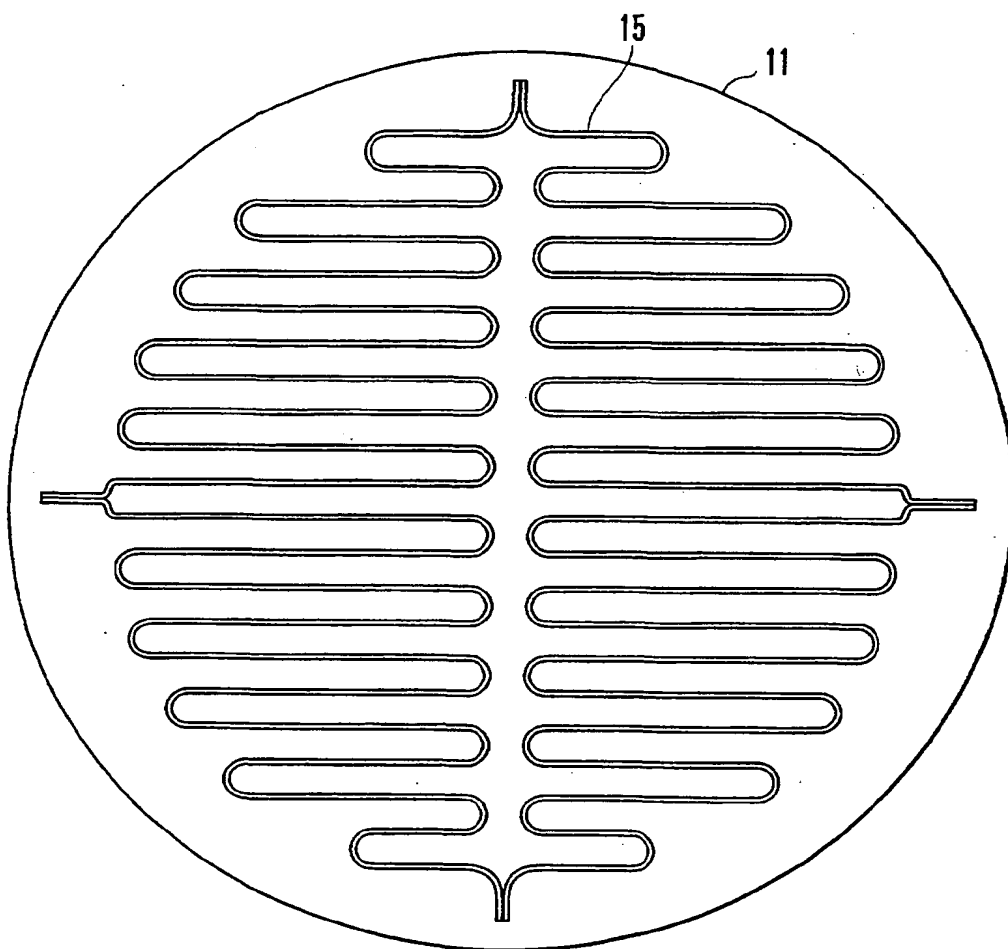


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/05406

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ H01L21/205, H01L21/31, C23C16/455		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ H01L21/205, H01L21/31, C23C16/455		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6126753 A (Tokyo Electron Limited), 03 October, 2000 (03.10.00), Fig. 9; column 15, lines 46 to 54 & JP 2000-87244 A Par. No. [0018]	1-4
Y	EP 909836 A2 (Ebara Corporation), 21 April, 1999 (21.04.99), column 2, lines 10 to 16 & US 6176929 B & JP 11-43773 A Par. Nos. [0004] to [0005]	1-4
Y	JP 3-122281 A (Anelva Corporation), 24 May, 1991 (24.05.91), Fig. 9; page 7, upper right column, line 2 to lower right column, line 7 (Family: none)	1-4
Y	JP 6-275530 A (NGK Insulators, Ltd.), 30 September, 1994 (30.09.94), Claim 1; Par. No. [0005]	3, 4
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 September, 2001 (14.09.01)		Date of mailing of the international search report 25 September, 2001 (25.09.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/05406

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, X	EP 1033743 A2 (Ebara Corporation), 06 September, 2000 (06.09.00), Full text & JP 2000-313961 A	1, 2
A	JP 8-291385 A (Tokyo Electron Limited), 05 November, 1996 (05.11.96), Figs. 1 to 2 (Family: none)	3, 4

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

